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(54) Title: METHOD FOR CONTROL OF AQUATIC VEGETATION

(57) Abstract: Protoporphyrinogen oxidase enzyme-inhibiting herbicides are useful in a method for controlling unwanted aquatic vegetation in a natural aquatic environment, such as in streams, ponds, rivers, lakes, and the like. Of particular interest is the use carfentrazone ethyl and certain metabolites thereof for control of aquatic algae and aquatic plants.

METHOD FOR CONTROL OF AQUATIC VEGETATION

This application claims the benefit of U.S. Provisional Application No. 60/473,601, filed May 27, 2003.

FIELD OF THE INVENTION

The present invention relates to the field of controlling unwanted plant species. In particular, the present invention relates to methods for controlling unwanted aquatic vegetation growing in or adjacent to bodies of water.

BACKGROUND OF THE INVENTION

Aquatic vegetation is found in most bodies of water, such as streams, rivers, lakes and ponds. Generally, aquatic vegetation is beneficial to the natural aquatic environment or ecosystem in moderate amounts. Such vegetation is needed, *inter alia*, for food production and cover for fish. Aquatic vegetation produces oxygen, stabilizes bottom sediment, protects the shoreline from wave erosion, and serves as feeding and nesting habitat for waterfowl. Aquatic vegetation, however, can become so abundant that it interferes with the use of that body of water for recreational purposes, such as swimming, fishing, and boating. An over abundance of aquatic vegetation can impede water flow in drainage ditches, irrigation channels, and culverts causing water to back up into areas where it is not wanted. An over abundance of aquatic vegetation can also create a hazard for aquatic life, offensive odors, and breeding grounds for mosquitoes. An over abundance of aquatic vegetation can also interfere with the flow of water in equipment transporting water, for example, for crop irrigation purposes. Irrigation, the controlled application of water for agricultural, or other purposes through man made systems to supply water requirements not satisfied by rainfall, is highly relevant to the farmer. For example, vegetables are 80 to 95 percent water. Because they contain so much water, their yield and quality suffer very quickly from lack of water. Thus, for good yields and high quality, irrigation is essential to the production of most vegetables.

Three methods of controlling unwanted aquatic vegetation that are widely used are mechanical, biological, and chemical methods.

Mechanical control of aquatic vegetation involves physically removing plants from the body of water. Hand pulling is effective to control cattails, willow trees and cottonwood trees while they are small. Raking is also used to remove algae and submerged vegetation in small areas in the body of water. Submerged vegetation also can be removed by pulling a chain or cable through the body of water between, for example, two tractors. Mechanical control is messy, time-consuming, temporary, and normally affects only a portion of the aquatic vegetation. It is the least effective method and may aggravate the problem since some aquatic plants spread through broken fragments and become new plants.

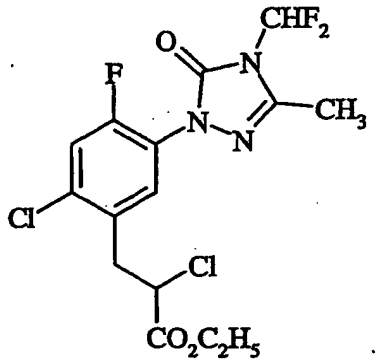
Biological control of aquatic vegetation includes the use of the triploid (sterile) carp, an herbivorous fish. However, they are expensive, may need to be restocked, and it may take up to three years to reduce the aquatic vegetation to an observable level through the use of this fish. In addition, the introduction of this fish into certain waters may require special permits. Ducks, geese and crayfish may be used to control aquatic vegetation. They produce inconsistent results, and some owners of waterways object to the mess waterfowl can make.

Chemical control of aquatic vegetation requires the application of a chemical, i.e., an herbicide, to the body of water where the aquatic vegetation is located. Herbicides known for use to control aquatic vegetation are copper sulfate, copper chelates, endothall, diquat, 2,4-D, fluridone, glyphosate, imazapyr, fluridone, and triclopyr (see for example http://www.rce.rutgers.edu/pubs/pdfs/fs386.pdf). There are considerable shortcomings in using the aforementioned herbicides for controlling aquatic vegetation. For example to name a few, some of these herbicides do not control both algae and aquatic plants; some have extended waiting periods of up to 30 days after treatment before the water can be used for irrigation; some should not be used at all if the water is to be used for irrigation, domestic use or watering livestock; some are toxic to fish; some are deleterious to desirable trees and shrubs growing along the banks of treated bodies of water.

Clearly, mechanical and biological methods of treatment are lacking in some respects for the control of aquatic vegetation; as well as are chemical treatment methods with the herbicides presently being used.

A newer class of herbicides different than those set forth above controls plants by disrupting certain functions in the plant cell. These herbicides are known

as inhibitors of the enzyme protoporphyrinogen oxidase (commonly known as PPO-inhibitors), which cause disruption of cell membranes by inducing lipid peroxidation resulting in death to the plant. An example of an herbicidal PPO-inhibitor is carfentrazone ethyl:



Carfentrazone-ethyl, namely ethyl α,2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoate, is disclosed and claimed in US Patent 5,125,958. Carfentrazone ethyl is known for its use in rice paddies to control weeds such as ricefield bulrush, small flower umbrellaplant, purple and redstem ammannia, and California arrowhead. Paddy rice is grown in a controlled aquatic environment, i.e., in paddies where tillage, planting, harvesting, and consistent management of water levels of about four to six inches occur throughout the growing season. In paddy rice, weed control by application of an herbicide is designed to maximize the yield of rice.

In contrast, a natural aquatic environment includes, without limitation, ponds, streams, lakes, rivers, irrigation channels, ditches and the like where there is no tillage or crop management processes being conducted that would change the ecosystem or environment. In such a natural aquatic environment there is a constant flux in the water level as well as a differential in the depth of the water.

SUMMARY OF THE INVENTION

In accordance with the present invention, it has now been found that certain protoporphyrinogen oxidase enzyme-inhibiting (PPO-inhibiting) herbicides are useful in controlling aquatic vegetation. Specifically, a method for controlling

unwanted aquatic vegetation in a natural aquatic environment has been found, which comprises applying an effective amount of one or more of a PPO-inhibiting herbicide, their agriculturally-acceptable salts, esters, acids, and metabolites to a locus where the aquatic vegetation is growing or is expected to grow. Other aspects of the present invention will become apparent from the description below.

DETAILED DESCRIPTION OF THE INVENTION

One aspect of the present invention relates to a method for controlling unwanted aquatic vegetation in a natural aquatic environment, which comprises applying an effective amount of one or more of a protoporphyrinogen oxidase enzyme-inhibiting herbicide, their agriculturally-acceptable salts, esters, acids, and metabolites to a locus where said vegetation is growing or is expected to grow.

Another aspect of the present invention relates to a method for obtaining water for purposes of irrigation that is free of debris such as displaced aquatic vegetation, where the water source is from a natural aquatic environment such as streams, rivers, lakes, ponds and the like. Specifically, it is a method of irrigating a crop with water, in which the method comprises:

i) controlling unwanted aquatic vegetation in a source of the water by application of an effective amount of one or more of a protoporphyrinogen oxidase enzyme-inhibiting herbicide, their agriculturally-acceptable salts, esters, acids, and metabolites to a locus where the vegetation is growing or is expected to grow;

and,

ii) transporting the water to a locus where a crop is growing or is expected to grow.

Aquatic vegetation controlled by methods of the present invention is classified into general categories based on its growth form and location. These classes generally include aquatic algae and aquatic plants. Aquatic algae are primitive plants having no true leaves or flowers. There are three categories of algae, *inter alia*, controlled by methods of the present invention; planktonic, filamentous, and attached-erect forms. Planktonic algae gives water a greenish-brown tint, but individual plants cannot be seen without a microscope. Filamentous algae, often referred to as "moss", or "pond scum" floats freely and forms greenish

mats on the surface of the water. The attached-erect forms often are mistaken for higher plants. This category of algae is characterized by its musky odor and gritty feel. Common examples of algae are spirogyra, cladophora, and chara, to name a few. Preferred in the context of the present invention are methods for control of green algae *Selenastrum capricornutum* Printz, marine diatom *Skeletonema costatum*, freshwater diatom *Navicula pelliculosa*, and blue-green algae *Anabaena flos-aquae*

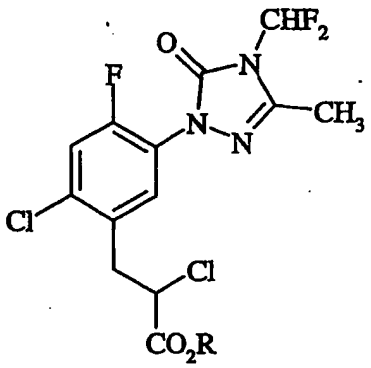
Aquatic plants are a higher order of plant life than algae. There are four categories of aquatic plants, *inter alia*, controlled by the methods of the present invention; marginal plants, submersed plants, emersed plants, and floating plants. Marginal plants are those that grow in the saturated soil on the waters edge, for example cattails. Submersed plants are true seed plants rooted on the bottom that mostly remain underwater, but a few flowers rise above the surface of the water, for example, southern and brittle naiads. Emersed plants are rooted on the bottom with floating leaves and flowers, for example, arrowhead and waterwillow. Floating plants are free-floating plants, or are rooted, but their leaves raise and fall with the water level, for example, duckweed and waterlilies. Other examples, of aquatic plants include, without limitation, American eloda, bladderwort, buttercup, cabomba, clasping-leaf pondweed, coontail, curly-leaf pondweed, eel grass, flat-stemmed pondweed, horned pondweed, leafy pondweed, sago pondweed, small pondweed, water milfoil, waterstargrass, common duckweed, star duckweed, water lettuce, water hyacinth, water pennywort, watermeal, American lotus, American pondweed, floating pondweed, Illinois pondweed, largeleaf pondweed, spatterdock, waterpurslane, watershield, waterthread pondweed, bulrush, bur reed, creeping water primrose, pickeralweed, purple loosestrife, spikerush, salvinia, water smartweed, willow, and other aquatic plants. Preferred in the context of the present invention are methods for control of duckweed, defined as *Lemna minor*, *Lemna trisulca*, and *Lemna gibba*, or more generally as *Lemna* sp.

As set forth above, certain PPO-inhibiting herbicides, their agriculturally-acceptable salts, esters, acids, and metabolites find utility in controlling unwanted aquatic vegetation when applied by the methods of the present invention to a locus where the aquatic vegetation is growing or is expected to grow. Examples of such PPO-inhibiting herbicides include, without limitation, one or more of acifluorfen-

sodium, aclonifen, bifenox, chlomethoxyfen, chlornitrofen, ethoxyfen-ethyl, fluorodifen, fluoroglycofen-ethyl, fluoronitrofen, fomesafen, furyloxyfen, halosafen, lactofen, nitrofen, nitrofluorfen, oxyfluorofen, cinidon-ethyl, flumiclorac-pentyl, flumioxazin, profluazol, pyrazogyl, oxadiargyl, oxadiazon, pentoxazone, fluazolate, pyraflufen-ethyl, benzfendizone, butafenacil, fluthiacet-methyl, thidiazimin, azafenidin, carfentrazone ethyl, sulfentrazone, flufenpyr-ethyl, as well as other PPO-inhibiting herbicides, and their agriculturally-acceptable salts, esters, acids, and metabolites. A preferred PPO-inhibiting herbicide for control of unwanted aquatic vegetation is carfentrazone ethyl and the metabolites of carfentrazone ethyl, namely, **i)** α,2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoic acid (chloropropanoic acid), **ii)** 2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropenoic acid (cinnamic acid), **iii)** 2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzoic acid (benzoic acid), and **iv)** 2-chloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoic acid (propanoic acid). A more preferred PPO-inhibiting herbicide for control of unwanted aquatic vegetation is carfentrazone ethyl. A most preferred embodiment of the present invention is that where the aquatic vegetation controlled is selected from *Selenastrum capricornutum*, *Skeletonema costatum*, *Navicula pelliculosa*, *Anabaena flos-aquae*, and *Lemna* sp.; and the PPO-inhibiting herbicide used for control of that aquatic vegetation is carfentrazone ethyl.

With proper dosage, the use of carfentrazone ethyl and the metabolites of carfentrazone ethyl, as set forth herein may provide selective herbicidal activity, thereby effectively controlling certain aquatic vegetation, such as algae and duckweed, and leaving certain less noxious aquatic vegetation, i.e., grasses such as cattails, relatively unaffected.

Other analogs, homologs or derivatives of carfentrazone ethyl that may find utility in the methods of the present invention include the following:



where R is selected from CH_3, $CH_2CH_2CH_3$, $CH(CH_3)_2$, $(CH_2)_3CH_3$, $CH_2CH(CH_3)_2$, n-pentyl, n-hexyl, Na^+, K^+, Li^+, Ca^+, and NH_4^+.

Carfentrazone ethyl, the metabolites, the analogs, homologs or derivatives set forth herein may be prepared by the methods taught in US patent 5,125,958 or by methods analogous thereto, or by methods known to one skilled in the art.

Under certain conditions it may be advantageous in the control of aquatic vegetation to combine an effective amount of one or more of the PPO-inhibiting herbicides of the present invention with a second herbicide. Of particular advantage may be the combination of one or more other herbicides that are known to have herbicidal activity on aquatic vegetation or are known for other uses, such as copper sulfate, copper chelates, endothall, diquat, 2,4-D, fluridone, glyphosate, imazapyr, fluridone, triclopyr, clomazone, hydrogen peroxide, paracetic acid, penoxsulam and bensulfuron. A preferable combination of PPO-inhibiting herbicide and herbicide known for activity on aquatic vegetation would be carfentrazone ethyl and one or more of copper sulfate, copper chelates, endothall, diquat, 2,4-D, fluridone, glyphosate, imazapyr, fluridone, triclopyr, clomazone, hydrogen peroxide, paracetic acid, penoxsulam and bensulfuron.

As used in this specification and unless otherwise indicated the terms "protoporphyrinogen oxidase enzyme-inhibiting", "protoporphyrinogen oxidase enzyme-inhibitor", "PPO- inhibiting", or "PPO-inhibitor" as these terms relate to the herbicides of the present invention as set forth herein are one and the same. The term "natural aquatic environment" refers to bodies of water, such as ponds, streams, lakes, rivers, irrigation channels, ditches and the like where there is no tillage or crop management processes being conducted that would change the ecosystem or environment. The term "irrigation" refers to the controlled application of water for

agricultural, or other purposes through man made systems to supply water requirements not satisfied by rainfall. The term "crop" refers to any and all vegetation propagated for use by man that may at times be in need of irrigation. The term "transporting" refers to any method employed by those skilled in the art to physically move water to a locus where its use is needed. The term "controlling" refers to the killing of, or minimizing the amount of aquatic vegetation to a point where it no longer poses a threat to clog waterways or equipment used for water handling.

One skilled in the art will, or course, recognize that the formulation and mode of application of a toxicant may affect the activity of the material in a given application. Thus, for use in the control of unwanted aquatic vegetation, the PPO-inhibiting herbicides finding utility in the present invention may be formulated as granules of relatively large particle size, as water-soluble or water-dispersible granules, as powdery dusts, as wettable powders, as emulsifiable concentrates, as solutions, or as any of several other known types of formulations, depending on the desired mode of application. It is to be understood that the amounts specified in this specification are intended to be approximate only, as if the word "about" were placed in front of the amounts specified.

These herbicidal compositions may be applied either as water-diluted sprays, or dusts, or granules to the areas in which suppression of vegetation is desired. These formulations may contain as little as 0.1%, 0.2% or 0.5% to as much as 95% or more by weight of active ingredient.

Dusts are free flowing admixtures of the active ingredient with finely divided solids such as talc, natural clays, kieselguhr, flours such as walnut shell and cottonseed flours, and other organic and inorganic solids which act as dispersants and carriers for the toxicant; these finely divided solids have an average particle size of less than about 50 microns. A typical dust formulation useful herein is one containing 1.0 part or less of the herbicidal compound and 99.0 parts of talc.

Wettable powders are in the form of finely divided particles, which disperse readily in water or other dispersant. The wettable powder is ultimately applied either as a dry dust or as an emulsion in water or other liquid. Typical carriers for wettable powders include Fuller's earth, kaolin clays, silicas, and other highly absorbent, readily wet inorganic diluents. Wettable powders normally are prepared

to contain about 5 - 80% of active ingredient, depending on the absorbency of the carrier, and usually also contain a small amount of a wetting, dispersing or emulsifying agent to facilitate dispersion. For example, a useful wettable powder formulation contains 80.0 parts of the herbicidal compound, 17.9 parts of Palmetto clay, and 1.0 part of sodium lignosulfonate and 0.3 part of sulfonated aliphatic polyester as wetting agents.

Other useful formulations for herbicidal applications are emulsifiable concentrates (ECs) which are homogeneous liquid compositions dispersible in water or other dispersant, and may consist entirely of the herbicidal compound and a liquid or solid emulsifying agent, or may also contain a liquid carrier, such as xylene, heavy aromatic naphthas, isphorone, or other non-volatile organic solvents. For herbicidal application these concentrates are dispersed in water or other liquid carrier and normally applied as a spray to the area to be treated. The percentage by weight of the essential active ingredient may vary according to the manner in which the composition is to be applied, but in general comprises 0.5 to 95% of active ingredient by weight of the herbicidal composition.

Flowable formulations are similar to ECs except that the active ingredient is suspended in a liquid carrier, generally water. Flowables, like ECs, may include a small amount of a surfactant, and will typically contain active ingredients in the range of 0.5 to 95%, frequently from 10 to 50%, by weight of the composition. For application, flowables may be diluted in water or other liquid vehicle, and are normally applied as a spray to the area to be treated.

Typical wetting, dispersing or emulsifying agents used in certain formulations include, but are not limited to, the alkyl and alkylaryl sulfonates and sulfates and their sodium salts; alkylaryl polyether alcohols; sulfated higher alcohols; polyethylene oxides; sulfonated animal and vegetable oils; sulfonated petroleum oils; fatty acid esters of polyhydric alcohols and the ethylene oxide addition products of such esters; and the addition product of long chain mercaptans and ethylene oxide. Many other types of useful surface - active agents are available in commerce. Surface-active agents, when used, normally comprise 1 to 15% by weight of the composition.

Still other useful formulations for herbicidal applications include simple solutions of the active ingredient in a solvent in which it is completely soluble at the

desired concentration, such as acetone, alkylated naphthalenes, xylene, or other organic solvents. Granular formulations, wherein the toxicant is carried on relative coarse particles, are of particular utility for aerial distribution or for penetration of a cover canopy. Pressurized sprays, typically aerosols wherein the active ingredient is dispersed in finely divided form as a result of vaporization of a low-boiling dispersant solvent carrier may also be used. Water-soluble or water-dispersible granules are free-flowing, non-dusty, and readily water-soluble or water-miscible. In use by the farmer on the field, the granular formulations, emulsifiable concentrates, flowable concentrates, solutions, etc., may be diluted with water to give a concentration of active ingredient in the range of say 0.1% or 0.2% to 1.5% or 2%.

The following examples further illustrate the present invention, but, of course, should not be construed as in any way limiting its scope. The examples are organized to present protocols for the evaluation of certain PPO-inhibiting herbicides when placed in contact with aquatic vegetation, and set forth certain biological data indicating the efficacy of such compounds.

Example 1
Test of Carfentrazone-ethyl on Duckweed (*Lemna gibba* G3)

A primary standard solution comprised of 2000 µg/mL of carfentrazone-ethyl was prepared by first weighing 0.0217 gram of technical carfentrazone-ethyl into a 10 mL volumetric flask, and bringing the volume to 10 mL with acetone. A 200 µg/mL secondary standard solution of carfentrazone-ethyl was prepared by injecting a 1.0 mL aliquot of the primary standard solution into a 10 mL volumetric flask, then bringing the volume to 10 mL with acetone. The 200 µg/mL secondary standard solution of carfentrazone-ethyl was then used to prepare a 20 µg/L solution by injecting 0.2 mL of the secondary standard solution into a sterile glass 2000 mL volumetric flask containing Hoaglands Nutrient Medium, then bringing the volume to 2000 mL with additional Hoaglands Nutrient Medium. From the 20 µg/L solution of carfentrazone ethyl, 1.3 µg/L, 2.5 µg/L, 5.0 µg/L and 10 µg/L samples of carfentrazone ethyl were prepared by transferring aliquots of 65 mL, 125 mL, 250 mL, and 500 mL, respectively, of the 20 µg/L test solution to sterile 1000 mL

volumetric flasks containing Hoaglands Nutrient Medium. Each flask was then brought to volume of 1000 mL with the Hoaglands Nutrient Medium.

The test of carfentrazone ethyl on duckweed (*Lemna gibba* G3) was conducted in at least three replicates for each rate of application on 10 day old duckweed that was obtained from USDA/ARS Beltsville Agricultural Research Center, Beltsville, MD. For each replicate, 200 mL each of the appropriate test solution as set forth above were placed in clean, sterile 500 mL Erlenmeyer flasks each equipped with a foam plug. A total of fifteen fronds of duckweed were then placed in each of the Erlenmeyer flasks. The flasks were then positioned in a random fashion using a computer-generated random table and incubated for 14 days at 25 °C ± 2 °C under 5010 lux ± 810 lux of continuous warm-white fluorescent light. A blank containing acetone only and a control containing the 20 µg/L test solution without duckweed were included in the test.

The measured concentrations of carfentrazone ethyl in the test samples were determined from samples of each test level and control collected on day 0. Analyses of these samples were conducted using high-pressure liquid chromatography with ultraviolet detection. At 0 day the measured concentrations of carfentrazone ethyl were 1.0 µg/L, 2.2 µg/L, 4.1 µg/L, 8.0 µg/L, and 13 µg/L; down from the 1.3 µg/L, 2.5 µg/L, 5.0 µg/L 10 µg/L, and 20 µg/L samples of carfentrazone ethyl, respectively, as initially prepared.

The number of duckweed fronds and condition in terms of necrosis, chlorosis, and frond death in each replicate was determined on 0 days, 2 days, 4 days, 7 days, 9 days, 11 days, and 14 days after initiation of the test. Chlorotic fronds were defined as fronds possessing areas of progressive bleaching in color from green to yellow. Fronds noted as necrotic possessed localized regions of dead or decaying tissue, usually surrounded by healthy tissue. Those fronds possessing only all brown or white tissue were considered dead. Fronds possessing no chlorotic or necrotic characteristics were considered normal. Every frond that was visibly projecting beyond the edge of the parent frond was counted. The counts were made at approximately the same time each day of observation. The results follow:

Table 1
Frond Observations in Duckweed (*Lemna gibba* G3)
During Exposure to Carfentrazone Ethyl

Conc. (µg/L)	Number and Condition of Fronds at Days of Exposure to Carfentrazone Ethyl						
	0 Day[1]	2 Day[1]	4 Day[1]	7 Day[1]	9 Day[1]	11 Day[1]	14 Day[1]
Blank[2]	15N	24N	44N, 0.3C	80N, 0.3C	134N, 0.3C, 0.3NF	201N, 0.3C	318N, 0.7C, 0.7NF
1.0	15N	25N	48N	87N	153N	216N, 0.3C	365N, 1C
2.2	15N	24N	49N	83N, 0.3C, 0.3NF	143N, 0.3C	215N	322N, 3C, 0.3NF
4.1	15N	21N	42N, 0.7C, 1NF	68N, 3.3C, 1NF	113N, 5.7C, 1NF	175N, 3C, 1.3NF	259N, 3.7C, 1.7NF, 0.3D
8.0	15N	15.3N, 4.3NF	16N, 5.3C, 3.7NF	29N, 4.7C, 4NF, 2D	41N, 5.7C, 3.7NF, 3.7D	46N, 5.3C, 5NF, 3D	81N, 5.7C, 4NF, 20.7D
13.0	15N	11N, 4.7NF	3N, 2.7C, 4NF, 2.7D	4.3N, 4C, 2NF, 4.3D	4N, 3C, 1.7NF, 6.7D	4N, 3.3C, 2NF, 6.3D	2.7N, 4.3C, 2.3NF, 7D

[1]Average of at least three replicates; [2]Contains only water and solvent (acetone in this case) used to dissolve the test compound; N = normal fronds; C = chlorotic fronds; NF = Necrotic fronds; D = Dead fronds. Carfentrazone ethyl is ethyl α,2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoate.

Table 1A
Percent Reduction in Normal Fronds of Duckweed in Table 1
When Compared to The Blank

Conc. (µg/L)	Number of Normal Fronds/Percent Reduction of Normal Fronds						
	0 Day	2 Day	4 Day	7 Day	9 Day	11 Day	14 Day
Blank	15	24	44	80	134	201	318
	—	—	—	—	—	—	—
1.0	15	25	48	87	153	216	365
	—	—	—	—	—	—	—
2.2	15	24	49	83	143	215	322
	—	—	—	—	—	—	—
4.1	15	21	42	68	113	175	259
	—	12.5%	4.5%	15%	15.7%	12.9%	18.6%
8.0	15	15.3	16	29	41	46	8
	—	36.3%	63.7%	63.8%	69.4%	77.1%	97.5%
13.0	15	11	3	4.3	4	4	2.7
	—	54.2%	93.2%	94.6%	97.0%	98%	99.2%

As shown in Table 1A, derived from data presented in Table1, duckweed is being controlled at concentration rates as low as 4.1 μg/L of carfentrazone ethyl for periods of at least 14 days. For example, at a concentration of 4.1 μg/L of carfentrazone ethyl, duckweed was reduced by about 19% at 14 days after exposure. At the higher concentration rate of 13 μg/L of carfentrazone ethyl, duckweed was nearly eradicated, being reduced by about 99% at 14 days after exposure.

Example 2
Test of Carfentrazone-ethyl in Admixture with Two of its Metabolites on Duckweed (*Lemna gibba* G3)

This test was done in a manner analogous to that set forth in Example 1. The test was conducted on *Lemna gibba* G3 with carfentrazone ethyl in admixture with two of its metabolites, namely α,2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoic acid (chloropropanoic acid), and 2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropenoic acid (cinnamic acid). The test mixture was comprised of three parts of carfentrazone ethyl (0.5 μg/L), eight parts of chloropropanoic acid (1.35 μg/L), and one part of cinnamic acid (0.17 μg/L) (3:8:1) Various concentrations of the test combination were tested. The results follow:

Table 2
Frond Observations in Duckweed (*Lemna gibba* G3) During Exposure to Carfentrazone Ethyl in Admixture with its Metabolites A[3] and B[4]

Conc. (µg total 3:8:1/L[5])	Number and Condition of Fronds at Days of Exposure to Carfentrazone Ethyl in Admixture with its Metabolites A and B						
	0 Day[1]	2 Day[1]	5 Day[1]	7 Day[1]	9 Day[1]	12 Day[1]	14 Day[1]
Blank[2]	17N	20.7N	42.3N, 1.7C	50N, 2.7C	71.7N, 1.3NC	89.3N, 1.3C, 1.7D	109N, 2.3NC, 1.7D
1.6	17N	18.7N, 0.3C	36.3N, 2.7C	46.7N, 2.3C, 0.7D	60N, 1NC, 1.7C, 0.3D	80.3N, 0.3NC, 3D	97.7N, 0.7NC, 1.3C, 3.7D
3.1	17N	22.3N, 0.3C	42N, 2.7C	54N, 3C	70N, 1.7NC, 0.3C, 0.7D	91N, 1.7NC, 2D	108.3N, 0.7NC, 0.7C, 3D
6.3	17N	21.7N, 1C	44.7N, 3C	57.7N, 1.7C, 0.3D	74N, 1.3NC, 1D	95.3N, 1C, 0.7NC, 1.7D	118.7N, 0.7NC, 1.3C, 2D
13	17N	19.3N, 0.7C	35N, 2C	42.3N, 0.3NC, 2.3C, 0.3D	58.3N, 0.3NC, 2.7C, 0.7D	77N, 1.7NC, 1C, 2D	97.3N, 1.3NC, 1.3C, 2.3D
25	17N	20.3N, 0.3C	34N, 2.3C	46N, 0.7NC, 2.3C, 0.3D	62.3N, 1NC, 1C, 0.3D	98.7N, 0.7NC, 0.3C, 1.7D	121.3N, 1.7NC, 1C, 2.7D
50	17N	15.7N, 2.3C	21.3N, 4.7C, 0.7D	26.7N, 2NC, 3.7C, 0.3D	28N, 2.3NC, 3C, 1D	30N, 4.3NC, 2C, 1.3D	41N, 5.7NC, 3.3C, 1.7D
100	17N	15N, 2.3C	9.7N, 8C	9.3N, 2.7NC, 4.7C, 1D	9.3N, 5.7NC, 1.7C, 1D	0N, 6.7NC, 1C, 1D	0N, 12.7NC, 2.3C, 2.7D

[1]Average of at least three replicates; [2]Contains only water and solvent (acetone in this case) used to dissolve the test compound; N = Normal fronds; NC = necrotic fronds; C = chlorotic fronds; D = Dead fronds; [3]α,2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoic acid (chloropropanoic acid); [4]2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropenoic acid (cinnamic acid). [5]3:8:1 ratio is carfentrazone ethyl : chloropropanoic acid : cinnamic acid, respectively.

Table 2A
Percent Reduction in Normal Fronds of Duckweed in Table 2
When Compared to The Blank

Conc. (µg total 3:8:1/L)	Number of Normal Fronds/Percent Reduction of Normal Fronds						
	0 Day	2 Day	4 Day	7 Day	9 Day	11 Day	14 Day
Blank	17	20.7	42.3	50	71.7	89.3	109
	—	—	—	—	—	—	—
1.6	17	18.7	36.3	46.7	60	80.3	97.7
	—	9.7%	14.2%	6.6%	16.3%	10.1%	10.4%
3.1	17	22.3	42	54	70	91	108.3
	—	—	0.7%	—	2.4%	—	0.6%
6.3	17	21.7	44.7	57.7	74	95.3	118.7
	—	—	—	—	—	—	—
13	17	19.3	35	42.3	58.3	77	97.3
	—	6.8%	17.3%	15.4%	18.7%	13.8%	10.7%
25	17	20.3	34	46	62.3	98.7	121.3
	—	1.9%	7.1%	8.0%	13.1%	—	—
50	17	15.7	21.3	26.7	28	30	41
	—	24.2%	49.6%	46.6%	60.9%	66.4%	62.4%
100	17	15	9	9.3	9.3	0	0
	—	27.5%	78.7%	81.4%	87.0%	100%	100%

As shown in Table 2A, derived from data presented in Table 2, duckweed is responding to the mixture of carfentrazone-ethyl-metabolites mixture, but is erratic at the lower concentration rates. At the higher concentration rates of the carfentrazone ethyl-metabolites mixture, control of duckweed is improved greatly. For example, at the higher concentration rate of 100 µg/L of carfentrazone ethyl-metabolites mixture, duckweed was reduced by about 80% at 4 days after exposure.

Example 3
Test of Carfentrazone-ethyl on Green Algae (*Selenastrum capricornutum* Printz)

A primary standard comprised of 320 µg/mL of carfentrazone-ethyl was prepared by adding 0.0349 gram of carfentrazone-ethyl to 100 mL of acetone. A 0.20 mL aliquot of the primary standard was added to 2000 mL of an algal nutrient

medium to prepare a 0.032 µg/mL working standard. Serial dilutions of the 32 µg/L standard were done by placing aliquots of 31.2 mL, 62.5 mL, 125 mL, 250 mL, and 500 mL of the standard into 1000 mL volumetric flasks and diluting to 1000 mL with a sterile algal test medium to provide test concentrations of carfentrazone-ethyl of 1.0 µg/L, 2.0 µg/L, 4.0 µg/L, 8.0 µg/L, 16 µg/L, and 32 µg/L, respectively.

The test of carfentrazone ethyl on green algae (*Selenastrum capricornutum* Printz) was conducted in at least three replicates for each rate of application on green algae obtained from The Department of Botany, Culture Collection of Algae, University of Texas at Austin, Austin, Texas. For each replicate, 100 mL each of the appropriate test solution as set forth above were placed in clean, sterile 250 mL Erlenmeyer flasks each equipped with a foam plug. A 5.5 mL aliquot of *Selenastrum capricornutum* Printz was pipetted into each of the test flasks. Each 5.5 mL aliquot contained a cell count of about 0.33 x 10^{-3} cells of algae/mL of algal nutrient, as determined with a hemacytometer and an Olympus Model BH-2 microscope. The flasks were then positioned in a random fashion, incubated for 120 hours at 24 °C ± 2 °C under about 4300 lux of continuous warm-white fluorescent light, and oscillated at about 100 rpm. A blank containing acetone and algal nutrient only was included in the test.

The measured concentrations of carfentrazone ethyl in the test samples were determined from samples of each test level and control collected on 0 hour. Analyses of these samples were conducted using high-pressure liquid chromatography with ultraviolet detection. At 0 hour the measured concentrations of carfentrazone ethyl were unexplainably higher than in the test samples as originally prepared.

Cell counts of *Selenastrum capricornutum* Printz were conducted at 0 hour, 24 hours, 48 hours, 72 hours, 96 hours, and 120 hours for each replicate and controls using the aforementioned hemacytometer and microscope. The results follow:

Table 3
Inhibition of Cell Counts of Green Algae *Selenastrum capricornutum* Printz During Exposure to Carfentrazone Ethyl

Conc. (µg/L)	Cell Counts (x 10^4 Cells/mL) / Percent Inhibition Compared to The Blank[1]					
	0-Hour[2]	24-Hour[2]	48-Hour[2]	72-Hour[2]	96-Hour[2]	120-Hour[2]
Blank[3]	0.33	0.74	2.6	6.0	30	120
	—	—	—	—	—	—
1.0	—	0.67	2.3	6.7	29	130
		9.5%	11.5%	—	3.2%	—
2.0	—	0.71	2.7	6.2	29	140
		4.1%	—	—	3.2%	—
4.0	—	0.71	1.7	5.9	26	140
		4.1%	34.6%	1.7%	13.3%	—
8.0	—	0.67	1.7	5.8	26	150
		9.5%	34.6%	3.3%	13.3%	—
16	—	0.44	1.2	4.2	19	87
		34.3%	47.8%	37.3%	34.5%	33.1%
32	—	0.29	0.74	1.4	0.71	2.1
		56.7%	67.8%	79.1%	97.6%	98.4%

[1]Average of at least three replicates; [2]The amount of time *Selenastrum capricornutum* Printz was exposed to carfentrazone ethyl; [3]Contains all ingredients except the test compound.

As shown in Table 3, Carfentrazone ethyl has an effect on *Selenastrum capricornutum* Printz at concentration rates as low as 1.0 µg/L, albeit erratic. At the higher concentration rates of application, carfentrazone ethyl provides very good control of this alga. For example, at a concentration rate of 32 µg/L, carfentrazone ethyl inhibits the cell count of *Selenastrum capricornutum* Printz by about 70% at 48 hours after exposure.

Example 4
Test of Carfentrazone-ethyl on Marine Diatom *Skeletonema costatum*

This test was done in a manner analogous to that set forth in Example 3, using the marine diatom *Skeletonema costatum*. The results follow:

Table 4
Inhibition of Cell Counts of Marine Diatom *Skeletonema costatum* During Exposure to Carfentrazone Ethyl

Conc. (µg/L)	Cell Counts (x 10^4 Cells/mL) / Percent Inhibition Compared to The Blank[1]					
	0-Hour[2]	24-Hour[2]	48-Hour[2]	72-Hour[2]	96-Hour[2]	120-Hour[2]
Blank[3]	1.2	2.7	2.5	5.5	6.1	46
	—	—	—	—	—	—
10	—	1.2	1.1	4.2	5.7	51
		55.6%	56.0%	23.6%	6.6%	—
18	—	2.5	0.85	2.0	0.48	1.6
		7.4%	66.0%	60.0%	92.1%	96.5%
41	—	2.6	0.52	0.41	0	0
		3.7%	79.2%	92.5%	100%	100%
70	—	0.59	0.70	0.52	0	0
		78.1%	72.0%	90.5%	100%	100%
137	—	0.56	0.15	0.22	0	0
		79.3%	94.0%	96.0%	100%	100%

[1]Average of at least three replicates; [2]The amount of time *Skeletonema costatum* was exposed to carfentrazone ethyl; [3]Contains all ingredients except the test compound.

As shown in Table 4, Carfentrazone ethyl has very good control of *Skeletonema costatum* at concentration rates as low as 18 µg/L. At the higher concentration rates of application, carfentrazone ethyl eradicates this alga. For example, at a concentration rate of 41 µg/L, carfentrazone ethyl inhibits the cell count of *Skeletonema costatum* by 100% at 96 hours after exposure.

Example 5
Test of Carfentrazone-ethyl on The Freshwater Diatom *Navicula pelliculosa*

This test was done in a manner analogous to that set forth in Example 3, using the freshwater diatom *Navicula pelliculosa*. The results follow:

Table 5
Inhibition of Cell Counts of Freshwater Diatom *Navicula pelliculosa* During Exposure to Carfentrazone Ethyl

Conc. (µg/L)	Cell Counts (x 10^4 Cells/mL) / Percent Inhibition Compared to The Blank[1]					
	0-Hour[2]	24-Hour[2]	48-Hour[2]	72-Hour[2]	96-Hour[2]	120-Hour[2]
Blank[3]	0.33	1.4	0.66	1.9	8.1	27
	—	—	—	—	—	—
1.9	—	1.0	1.3	2.5	9.4	35
		—	—	—	—	—
2.6	—	0.85	1.2	1.9	4.6	16
		39.3%	—	—	43.2%	40.7%
4.8	—	0.74	0.70	1.7	5.8	18
		47.1%	—	10.5%	28.4%	33.3%
9.4	—	0.78	0.48	0.96	3.1	11
		44.3%	27.3%	49.5%	61.7%	59.3%
21	—	0.56	0.85	0.56	2.2	4
		60.0%	—	70.5%	72.8%	85.2%

[1]Average of at least three replicates; [2]The amount of time *Navicula pelliculosa* was exposed to carfentrazone ethyl; [3]Contains all ingredients except the test compound. .

As shown in Table 5, Carfentrazone ethyl has an effect on *Navicula pelliculosa* at concentration rates as low as 2.6 µg/L. At the higher concentration rates of application, carfentrazone ethyl provides good control of this alga. For example, at a concentration rate of 21 µg/L, carfentrazone ethyl inhibits the cell count of *Navicula pelliculosa* by about 85% at 120 hours after exposure.

Example 6
Test of Carfentrazone-ethyl on The Blue-Green Algae *Anabaena flos-aquae*

This test was done in a manner analogous to that set forth in Example 3, using the blue-green algae *Anabaena flos-aquae*. The results follow:

Table 6
Inhibition of Cell Counts of Blue-Green Algae *Anabaena flos-aquae* During Exposure to Carfentrazone Ethyl

Conc. (µg/L)	Cell Counts (x 10^4 Cells/mL) / Percent Inhibition Compared to The Blank[1]					
	0-Hour[2]	24-Hour[2]	48-Hour[2]	72-Hour[2]	96-Hour[2]	120-Hour[2]
Blank[3]	0.40	2.1	5.8	16	47	160
	—	—	—	—	—	—
1.2	—	2.2	4.7	17	53	150
		—	19.0%	—	—	6.3%
2.0	—	1.4	4.2	17	55	150
		33.3%	27.6%	—	—	6.3%
4.8	—	0.82	4.1	11	43	120
		61.0%	29.3%	31.3%	8.5%	25.0%
10	—	0.74	3.0	11	29	110
		64.8%	48.3%	31.3%	38.3%	31.3%
18	—	0.89	1.3	5.2	26	71
		57.6%	77.6%	67.5%	44.7%	55.6%

[1]Average of at least three replicates; [2]The amount of time *Anabaena flos-aquae* was exposed to carfentrazone ethyl; [3]Contains all ingredients except the test compound.

As shown in Table 6, Carfentrazone ethyl has an effect on *Anabaena flos-aquae* at concentration rates as low as 1.2 µg/L. At the higher concentration rates of application, carfentrazone ethyl provides good control of this alga. For example, at a concentration rate of 18 µg/L, carfentrazone ethyl inhibits the cell count of *Anabaena flos-aquae* by about 78% at 48 hours, about 45% at 96 hours, and about 56% at 120 hours after exposure.

As set forth in the following examples, certain metabolites of carfentrazone were tested for algaecidal activity against the green algae *Selenastrum capricornutum* Printz. The metabolites tested were i) α,2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoic acid (chloropropanoic acid-designated Metabolite A); ii) 2-chloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropenoic acid (cinnamic acid-designated Metabolite B); iii) 2-

dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzoic acid (benzoic acid-designated Metabolite C); and, iv) 2-chloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoic acid (propanoic acid-designated Metabolite D).

Example 7
Test of Carfentrazone-ethyl Metabolite A on Green Algae (*Selenastrum capricornutum* Printz)

This test was done in an analogous manner to that set forth in Example 3. The results follow:

Table 7
Inhibition of Cell Counts of Green Algae *Selenastrum capricornutum* Printz During Exposure to Carfentrazone Ethyl Metabolite A[1]

	Cell Counts (x 10^4 Cells/mL) / Percent Inhibition Compared to The Blank[2]			
Conc. (µg/L)	0-Hour[3]	24-Hour[3]	48-Hour[3]	72-Hour[3]
Blank[4]	1 —	2.1 —	13.1 —	44.5 —
53	1 —	2.3 —	13.9 —	50.5 —
95	1 —	2.1 —	12.1 7.6%	53.1 —
199	1 —	2.3 —	11.9 9.2%	52.1 —
405	1 —	1.5 28.6%	10.5 19.8%	43.1 3.1%
801	1 —	1.1 47.6%	1.6 87.8%	5.5 87.7%
1610	1 —	1 52.4%	1 92.4%	1 97.8%

[1]Carfentrazone ethyl Metabolite A is α,2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoic acid (chloropropanoic acid); [2]Average of at least three replicates; [3]The amount of time *Selenastrum capricornutum* Printz was exposed to carfentrazone ethyl-Metabolite A; [4]Contains all ingredients except the test compound.

As shown in Table 7, carfentrazone ethyl Metabolite A provides control of *Selenastrum capricornutum* Printz, but at concentration rates considerably higher than carfentrazone ethyl. For example, at a concentration rate of 801 µg/L, Metabolite A inhibits the cell count of *Selenastrum capricornutum* Printz by about 88% at 72 hours after exposure.

Example 8
Test of Carfentrazone-ethyl Metabolite B on
Green Algae (*Selenastrum capricornutum* Printz)

This test was done in a manner analogous to that set forth in Example 3. The results follow:

Table 8

Inhibition of Cell Counts of Green Algae *Selenastrum capricornutum* Printz During Exposure to Carfentrazone Ethyl Metabolite B[1]

	Cell Counts (x 10^4 Cells/mL) / Percent Inhibition Compared to The Blank[2]			
Conc. (µg/L)	0-Hour[3]	24-Hour[3]	48-Hour[3]	72-Hour[3]
Blank[4]	—	2.7	15.4	96.6
		—	—	—
8.5	—	2.6	18.9	110
		3.7%	—	—
16.7	—	2.1	11.3	66.3
		22.2%	26.6%	31.4%
36.1	—	1.6	7.0	39.8
		40.7%	54.5%	58.8%
76.7	—	1.1	1.8	3.9
		59.3%	88.3%	95.9%
146	—	1.0	1.9	0.5
		63.0%	87.7%	99.5%

[1]Carfentrazone ethyl Metabolite B is 2-chloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropenoic acid (cinnamic acid); [2]Average of at least three replicates; [3]The amount of time *Selenastrum capricornutum* Printz was exposed to carfentrazone ethyl-Metabolite B; [4]Contains all ingredients except the test compound.

As shown in Table 8, carfentrazone ethyl Metabolite B provides control of *Selenastrum capricornutum* Printz, but at concentration rates somewhat higher than

carfentrazone ethyl. For example, at a concentration rate of 76.7 µg/L, Metabolite B inhibits the cell count of *Selenastrum capricornutum* Printz by about 88% at 48 hours after exposure.

Example 9
Test of Carfentrazone-ethyl Metabolite C on Green Algae (*Selenastrum capricornutum* Printz)

This test was done in a manner analogous to that set forth in Example 3. The results follow:

Table 9
Inhibition of Cell Counts of Green Algae *Selenastrum capricornutum* Printz During Exposure to Carfentrazone Ethyl Metabolite C[1]

	Cell Counts (x 10^4 Cells/mL) / Percent Inhibition Compared to The Blank[2]			
Conc. (µg/L)	0-Hour[3]	24-Hour[3]	48-Hour[3]	72-Hour[3]
Blank[4]	1 —	2.7 —	11.8 —	52.1 —
2.7 x 10^3	1 —	1.9 29.6%	10.2 13.6%	50.5 3.1%
5.14 x 10^3	1 —	2.1 22.2%	11.6 1.7%	49.1 5.8%
11.2 x 10^3	1 —	2.7 —	9.0 23.7%	39.1 25.0%
22.6 x 10^3	1 —	2.2 18.5%	3.3 72.0%	3.8 92.7%
46.0 x 10^3	1 —	2.0 25.9%	1.1 90.7%	1.7 96.7%
91.1 x 10^3	1 —	1.0 63.0%	1.0 91.5%	1.0 98.1%

[1]Carfentrazone ethyl Metabolite C is 2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzoic acid (benzoic acid); [2]Average of at least three replicates; [3]The amount of time *Selenastrum capricornutum* Printz was exposed to carfentrazone ethyl-Metabolite C; [4]Contains all ingredients except the test compound.

As shown in Table 9, carfentrazone ethyl Metabolite C provides control of *Selenastrum capricornutum* Printz, but at concentration rates extremely high when

compared to carfentrazone ethyl. For example, at a concentration rate of 22.6 x 10^3 µg/L, Metabolite C inhibits the cell count of *Selenastrum capricornutum* Printz by about 93% at 72 hours after exposure.

Example 10
Test of Carfentrazone-ethyl Metabolite D on Green Algae (*Selenastrum capricornutum* Printz)

This test was done in a manner analogous to that set forth in Example 3. The results follow:

Table 10
Inhibition of Cell Counts of Green Algae *Selenastrum capricornutum* Printz During Exposure to Carfentrazone Ethyl Metabolite D[1]

	Cell Counts (x 10^4 Cells/mL) / Percent Inhibition Compared to The Blank[2]			
Conc. (µg/L)	0-Hour[3]	24-Hour[3]	48-Hour[3]	72-Hour[3]
Blank[4]	1	2.2	12.5	62.1
	—	—	—	—
54	1	2.3	12.9	62.3
	—	—	—	—
100	1	2.3	12.2	57.7
	—	—	2.4%	7.1%
202	1	1.8	1.9	3.1
	—	18.2%	84.8%	95.0%
390	1	1.3	1.0	1.0
	—	40.9%	92.0%	98.4%
778	1	1.0	1.0	1.0
	—	54.5%	92.0%	98.4%

[1]Carfentrazone ethyl Metabolite D is 2-chloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoic acid (propanoic acid); [2]Average of at least three replicates; [3]The amount of time *Selenastrum capricornutum* Printz was exposed to carfentrazone ethyl-Metabolite D; [4]Contains all ingredients except the test compound.

As shown in Table 10, carfentrazone ethyl Metabolite D provides control of *Selenastrum capricornutum* Printz, but at concentration rates higher than carfentrazone ethyl. For example, at a concentration rate of 202 µg/L, Metabolite D

inhibits the cell count of *Selenastrum capricornutum* Printz by about 95% at 72 hours after exposure.

While this invention has been described with an emphasis upon preferred embodiments, it will be understood by those of ordinary skill in the art that variations of the preferred embodiments may be used and that it is intended that the invention may be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications encompassed within the spirit and scope of the invention as defined by the following claims.

What is claimed is:

1. A method for controlling unwanted aquatic vegetation in a natural aquatic environment, which comprises applying an effective amount of one or more of a protoporphyrinogen oxidase enzyme-inhibiting herbicide, their agriculturally-acceptable salts, esters, acids, and metabolites to a locus where said vegetation is growing or is expected to grow.

2. The method of claim 1, wherein said aquatic vegetation is selected from aquatic algae and aquatic plants.

3. The method of claim 2, wherein said aquatic algae is selected from planktonic, filamentous, and attached-erect forms of aquatic algae.

4. The method of claim 3, wherein said aquatic algae is selected from *Selenastrum capricornutum*, *Skeletonema costatum*, *Navicula pelliculosa*, and *Anabaena flos-aquae*.

5. The method of claim 2, wherein said aquatic plants are selected from marginal, submersed, emersed, and floating aquatic plants.

6. The method of claim 5, wherein said aquatic plant is *Lemna* sp.

7. The method of claim 1, wherein said protoporphyrinogen oxidase enzyme-inhibiting herbicide is selected from one or more of acifluorfen-sodium, aclonifen, bifenox, chlomethoxyfen, chlornitrofen, ethoxyfen-ethyl, fluorodifen, fluoroglycofen-ethyl, fluoronitrofen, fomesafen, furyloxyfen, halosafen, lactofen, nitrofen, nitrofluorfen, oxyfluorofen, cinidon-ethyl, flumiclorac-pentyl, flumioxazin, profluazol, pyrazogyl, oxadiargyl, oxadiazon, pentoxazone, fluazolate, pyraflufen-ethyl, benzfendizone, butafenacil, fluthiacet-methyl, thidiazimin, azafenidin, carfentrazone ethyl, sulfentrazone, flufenpyr-ethyl, their agriculturally-acceptable salts, esters, acids, and metabolites.

8. The method of claim 7, wherein said protoporphyrinogen oxidase enzyme-inhibiting herbicide is selected from one or more of carfentrazone ethyl and metabolites of carfentrazone ethyl, wherein said metabolites are **i)** α,2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoic acid, **ii)** 2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropenoic acid, **iii)** 2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzoic acid, and **iv)** 2-chloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoic acid.

9. The method of claim 8, wherein said protoporphyrinogen oxidase enzyme-inhibiting herbicide is carfentrazone ethyl.

10. The method of claim 1, wherein said aquatic vegetation is selected from *Selenastrum capricornutum, Skeletonema costatum, Navicula pelliculosa, Anabaena flos-aquae,* and *Lemna* sp.; and said protoporphyrinogen oxidase enzyme-inhibiting herbicide is carfentrazone ethyl.

11. The method of claim 1, wherein said protoporphyrinogen oxidase enzyme-inhibiting herbicide is combined with a second herbicide.

12. The method of claim 11, wherein said second herbicide is selected from copper sulfate, copper chelates, endothall, diquat, 2,4-D, fluridone, glyphosate, imazapyr, fluridone, triclopyr, clomazone, hydrogen peroxide, paracetic acid, penoxulam and bensulfuron.

13. The method of claim 11, wherein said protoporphyrinogen oxidase enzyme-inhibiting herbicide is carfentrazone ethyl.

14. A method of irrigating a crop with water, wherein said method comprises:

i) controlling unwanted aquatic vegetation in a source of said water by application of an effective amount of one or

more of a protoporphyrinogen oxidase enzyme-inhibiting herbicide, their agriculturally-acceptable salts, esters, acids, and metabolites to a locus where said vegetation is growing or is expected to grow;
and,

ii) transporting said water to a locus where said crop is growing or is expected to grow.

15. The method of claim 14, wherein said aquatic vegetation is selected from aquatic algae and aquatic plants.

16. The method of claim 15, wherein said aquatic algae is selected from planktonic, filamentous, and attached-erect forms of aquatic algae.

17. The method of claim 16, wherein said aquatic algae is selected from *Selenastrum capricornutum*, *Skeletonema costatum*, *Navicula pelliculosa*, and *Anabaena flos-aquae*.

18. The method of claim 15, wherein said aquatic plants are selected from marginal, submersed, emersed, and floating aquatic plants.

19. The method of claim 18, wherein said aquatic plant is *Lemna* sp.

20. The method of claim 14, wherein said protoporphyrinogen oxidase enzyme-inhibiting herbicide is selected from one or more of acifluorfen-sodium, aclonifen, bifenox, chlomethoxyfen, chlornitrofen, ethoxyfen-ethyl, fluorodifen, fluoroglycofen-ethyl, fluoronitrofen, fomesafen, furyloxyfen, halosafen, lactofen, nitrofen, nitrofluorfen, oxyfluorofen, cinidon-ethyl, flumiclorac-pentyl, flumioxazin, profluazol, pyrazogyl, oxadiargyl, oxadiazon, pentoxazone, fluazolate, pyraflufen-ethyl, benzfendizone, butafenacil, fluthiacet-methyl, thidiazimin, azafenidin, carfentrazone ethyl, sulfentrazone, flufenpyr-ethyl, their agriculturally-acceptable salts, esters, acids, and metabolites.

21. The method of claim 20, wherein said protoporphyrinogen oxidase enzyme-inhibiting herbicide is selected from one or more of carfentrazone ethyl, and metabolites of carfentrazone ethyl, wherein said metabolites are **i)** α,2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoic acid, **ii)** 2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropenoic acid, **iii)** 2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzoic acid, and **iv)** 2-chloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoic acid.

22. The method of claim 21, wherein said protoporphyrinogen oxidase enzyme-inhibiting herbicide is carfentrazone ethyl.

23. The method of claim 14, wherein said aquatic vegetation is selected from *Selenastrum capricornutum*, *Skeletonema costatum*, *Navicula pelliculosa*, *Anabaena flos-aquae*, and *Lemna* sp; and said protoporphyrinogen oxidase enzyme-inhibiting herbicide is carfentrazone ethyl.

24. The method of claim 13, wherein said protoporphyrinogen oxidase enzyme-inhibiting herbicide is combined with a second herbicide.

25. The method of claim 24, wherein said second herbicide is selected from copper sulfate, copper chelates, endothall, diquat, 2,4-D, fluridone, glyphosate, imazapyr, fluridone, triclopyr, clomazone, hydrogen peroxide, paracetic acid, penoxsulam and bensulfuron.

26. The method of claim 24, wherein said protoporphyrinogen oxidase enzyme-inhibiting herbicide is carfentrazone ethyl.